

METHOD FOR OPERATING A MEMBRANE ELECTROCHEMICAL GENERATOR

BACKGROUND OF THE INVENTION

Fuel cells are known as devices for the direct conversion of the chemical energy of a fuel (such as pure hydrogen or hydrogen mixtures obtained by hydrocarbon steam reforming) to electric energy without involving a combustion step as instead occurs in the conventional generators based on the combustion-compressed vapour production-turbine expansion cycle or on the cycle comprising gas turbines. The absence of such combustion step sets the fuel cells free from the constraints of the known Carnot's principle and imparts them an intrinsically higher energy efficiency than the conventional generators.

Fuel cells can be divided into families depending on the operating temperature, which is 60-90°C for the proton-exchange membrane types (commonly identified as PEMFC), 180-250°C for the types making use of phosphoric acid as the electrolyte (PAFC), 600-700°C for the types in which the electrolyte consists of a mixture of molten carbonates (MCFC) and 800-1000°C for those in which the electrolyte is a solid state ion-conducting oxide (SOFC).

Whereas each type of fuel cells has its merits in terms of energy efficiency, promptness in following the power demand transients, start-up rapidity, maintenance in conditions of zero power generation, it's a matter of fact that the presence of liquid aggressive electrolytes (phosphoric acid, molten carbonates) or the high temperatures (600-1000°C) impose the use of sophisticated construction materials and particular measures in the design and operation, particularly as concerns the remarkable thermomechanical solicitations. For all these reasons, PAFC, MCFC and SPFC-type fuel cells are normally considered to be practically destined to the construction of big units with power exceeding 1 megawatt, such as for example distributed electric power plants, wherein the operation is subjected to transients of moderate entity and wherein some form of supervision by specialised personnel is available. Conversely, membrane fuel cells are substantially solid-state devices, hence free of the problems associated to

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corrosivity, as is the case with phosphoric acid and molten carbonates, to safety, since in the case of liquid electrolytes the separation of the fuel from the air reactant is ensured just by the capillary forces holding the electrolyte inside the pores of an inert matrix, and finally to the temperature as seen for the conductive solid oxides. Furthermore membrane fuel cells, being devices characterised by an extremely reduced electrode and membrane mass, have a particular capability of following steep power demands and of reaching the nominal power generation in very low times even starting from a zero generation condition. This set of characteristics makes fuel cells very attractive for their use in the automotive and also in the stationary field for small power applications, as is the case, very interesting from a commercial standpoint, of systems directed to be installed in private houses, hotels, hospitals.

Next to the positive characteristics illustrated, membrane fuel cells present however also some inconveniences: among these, particularly relevant is the need of having to maintain the proton-exchange membranes, whose conductivity is a function of the water content, in a fully hydrated state.

Membranes are usually 20 to 100 micron thick films consisting of a polymer on whose backbone groups with an acidic function, usually sulphonic groups, are inserted. The polymer must be resistant to the highly aggressive action of peroxidic and radicalic compounds generated as intermediate products of reaction of air. For this reason, the polymers currently used for the production of membranes presently available on the market as commercial or experimental products (best known suppliers: DuPont/USA, Asahi Glass/Japan, Asahi Kasei/Japan, Gore/Japan and Solvay Solexis/Italy) are invariably perfluorinated polymers characterised by high chemical inertia, even though a remarkable research activity is directed to the development of non-fluorinated polymers, for instance having an aromatic structure, whose long term chemical inertia and whose mass production scale economics have still to be demonstrated.

The acidic functions, and in particular the sulphonic groups, must be dissociated: the resulting free electric charge determines in fact a particular space orientation of the polymer chains with formation of reticular channels along which proton

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migration takes place. The dissociation, which is thus a required passage for channel formation, occurs only in the presence of certain water amounts, resulting in the need of keeping the membrane hydrated. The hydration condition is the outcome of a delicate equilibrium between water of reaction and water extracted from the gases flowing through the fuel cells during operation, in particular from the air and fuel respectively fed on the cathode side and on the anode side. The water extraction may become dangerously high for the membrane hydration when the fuel cell is operated at near-ambient pressure, hence with particularly elevated gas volumetric flow-rates. This situation is especially critical on the air side, since in order to maintain a sufficient oxygen partial pressure also in proximity of the cell outlet it is mandatory to operate with flow-rates substantially higher than the theoretical stoichiometric value, indicatively two-fold. On the hydrogen side the problem is less serious, since when operating with pure hydrogen the flow-rates must be practically correspondent to the theoretical values, aside from an excess of about 1% to guarantee the withdrawal of inerts which may otherwise accumulate: it is clear that such modest purge flow-rate extracts negligible amounts of water. The framework doesn't change significantly even when the fuel cell anode side is directly supplied with gas coming from the steam reforming unit which may contain, depending on the operative conditions, 50 to 75% hydrogen and which has a volumetric flow-rate indicatively equivalent up to 40-50% of the volumetric flow-rate of air. The capability of withdrawing water is further reduced due to the fact that the gas coming from the steam reforming unit is normally saturated with water vapour.

In the case of air, on the contrary, the water withdrawal capacity is high due both to the stoichiometric excess employed, resulting in a remarkable volumetric flow-rate particularly for the case of near-ambient pressure operation, and to the reduced moisture content present in the ambient air intake of fans or compressors used for the cell feeding. To correct this unfavourable situation, the prior art discloses various devices directed to saturate the air feed with water vapour at temperatures close to the fuel cell working temperature. The basic idea is in fact to eliminate the water-extracting capacity of air along the whole fuel cell crossing,

during which the air temperature rises anyway to values close to those of the cell. The saturation of air at temperatures close to cell temperature can be obviously achieved allowing the air to bubble in adequate external saturators consisting of vessels containing demineralised water kept at the desired temperature, for instance by thermal exchange with the water circulating inside the fuel cell: this procedure has the drawback of operating at an average temperature sensibly lower than that of the cell, as a consequence of the temperature differences required to reduce the thermal exchange surfaces. To carry out the saturation at temperatures close to that of the fuel cell it would then be necessary to resort to additional thermal energy sources with a consequent decrease of the energy efficiency of the overall system. The device moreover requires level control instrumentation, pumps for feeding water, purge flow-rate control to prevent the build up of impurities inevitably present, albeit in traces, in the water to be evaporated, coming from the condensation of vapour contained in the exhaust gases of the system before their release to the atmosphere, all of this involving non negligible additional costs. A similar procedure is claimed in US 6,350,535, wherein the air feed is added with atomised liquid water and the mixture so obtained is made progress across a heat exchanger whereto the required thermal energy for evaporating the water is provided. This device presents the same inconveniences discussed for the previous case.

In US 6,066,408 a humidification method is disclosed comprising humidification cells intercalated to the fuel cells of a stack: the humidification cells thereby work practically as cooling cell wherein the cooling is ensured by the evaporation of the water required to saturate the incoming air-flow. The humidification temperature results higher than that relative to the above discussed external saturators, although somehow lower than the fuel cell temperature since a certain thermal difference is in any case required to maintain an adequate heat exchange rate. With this type of device it is no more possible to employ additional heat sources to increase the humidification temperature until making it practically coincide with the cell temperature. The efficiency of the device is associated to the thermal level established in the stack, decreasing as the temperature decreases. The device is

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thus practically inactive during the start-up of the stack and during the periods of low power generation when the temperature is significantly lower than that of nominal operation.

In US 2001/0015501 the use of a unit generally defined as enthalpic unit is disclosed. This unit consists of a vessel subdivided into two compartments by a selective water-permeable membrane: the two compartments are supplied respectively with air at ambient temperature to be delivered to the stack and with water vapour-saturated hot exhaust air from the stack outlet. A heat and water exchange from the exhaust air to the air to be delivered to the stack, which is thereby heated and humidified, takes place through the membrane: also in this case, however, the final temperature of the air to be delivered to the stack is certainly lower than the fuel cell working temperature. This type of air-feed conditioning is acceptable in the case of pressurised operation, where the air volumetric flow-rate is substantially reduced and may have a temperature above ambient under the effect of compression, while being arguable and relatively less reliable for near-ambient pressure operation. A device functioning in a similar way is disclosed in DE 199 18 849 wherein the water and heat transfer does not take place through a selective membrane, but rather employing a rotating drum subdivided into sectors whose internal walls are provided with a film of hygroscopic material, for instance a lithium salt. The rotation of the drum puts each sector subsequently in communication first with the exhaust air that transfers its water content to the hygroscopic material and heat to the support structure, and then with the low-humidity air feed which heats up and extracts water from the hygroscopic material. This device suffers as well of the limitations mentioned for US 2001/0015501.

In US 5,441,821 it is proposed to ensure a certain humidification and temperature level through the recycle of the exhaust air to the air-feed fan or compressor: in this case, imagining that the exhaust air is saturated with water vapour, the humidity resulting from the overall air stream is a function of the ratio between the recycle and the environment air intake ("fresh" air) flow-rates. Since this ratio cannot be too large, in order to contain the fan or compressor size and the

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relevant energy consumption within reasonable limits, the overall air humidity content results to be not completely satisfactory, exactly as previously seen for the other kinds of devices. Furthermore the recycle of the oxygen-depleted exhaust air implies the oxygen average partial pressure inside the fuel cells being lower than the one characteristic of the recycle-free operation. This may entail some performance lessening.

To obviate to the above mentioned drawbacks and to meet the objective of ensuring a safe and complete membrane hydration, US 6,406,807 discloses a direct water injection inside the fuel cells: the evaporation effectively withdraws the heat generated during operation and at the same time generates the vapour partial pressure required to maintain a correct membrane hydration. This method still presents a remarkable critical point as that the water amounts have to be careful calibrated with respect to the power generation to prevent the two opposite risks of hydration loss (injection of insufficient amounts of water) and of flooding of the porous electrodes (injection of excessive amounts of water): all this requires injection pumps, water distributors inside the fuel cells and relevant controls, which besides implying additional costs introduce problems of functioning reliability as well.

A further way to face the problem of membrane dehydration is discussed in US 2002/0068214: in this case, besides the humidification carried out with one of the above described processes, the electrode in contact with the membrane is provided with reduced porosity in the air inlet region, which experience has shown being the most exposed to the risks of excessive water evaporation. In this way, water diffusion in the vapour or even in the liquid phase results the more hindered the lower is the residual porosity and consequently the water-to-air transfer also results slowed down, with a better preservation of membrane hydration. This procedure entails two serious inconveniences, one associated to the simultaneous restraint of the oxygen diffusion velocity accompanied by a performance loss, the other associated to the more complex electrode structure hardly in accordance with the low cost mass production requirements.

OBJECTS OF THE INVENTION

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It is an object of the present invention to overcome the limitations relative to the prior art.

In a first aspect of the invention the stable operation of membrane fuel cells, single or arranged in stacks, is obtained by cooling the non-humidified air feed to an adequate temperature.

In a second aspect of the invention the cooling of the non-humidified air feed is obtained by means of a suitable unit consisting of a fan or compressor followed by a heat exchanger wherein heat is extracted making use of ambient air as the coolant, followed in its turn by an expander wherein the air pressure is reduced down to the level required for achieving the desired thermal level.

In a third aspect of the invention the expander is connected to the fan or compressor so as to achieve a partial recovery of energy.

DESCRIPTION OF THE INVENTION

These aspects, together with other features of the device of the invention and of the functioning thereof are discussed in detail in the following section of text with the relevant figures, listed hereafter:

- Figure 1: cell voltage (indicating the energy conversion efficiency) and power as functions of the current density for a fuel cell fed with non pre-humidified cooled air according to the invention.
- Figure 2: comparison of the data of figure 1 with those relative to a fuel cell fed with pre-humidified warm air according to the indications of the prior art.
- Figure 3: maximum allowable exhaust air outlet temperatures as a function of the working pressure for a fuel cell fed with non pre-humidified cooled air according to the invention.
- Figure 4: stoichiometric factor as a function of the maximum exhaust air outlet temperature and of the working pressure.
- Figure 5: executive layout of the device of the invention.
- Figure 6: compression work multiplier as a function of ambient air temperature and of the working pressure.

During the operation of a fuel cell, single or arranged as a multiplicity of cells in a stack, the region of membrane most exposed to the risk of dehydration is the one

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immediately adjacent to the inlet of gases, and in particular to the air inlet to which future reference will be made hereafter. This region, in fact, is subject to a quick evaporation of the product water generated by the reaction between the air itself, the proton migrating across the membrane and the electrons flowing through the external circuit. If the rate of evaporation is higher than that of water formation the membrane undergoes a progressive dehydration hindering the proton migration with a consequent conductivity and performance loss. It must be noted that if the dehydration or scarce hydration situation persists in time, the polymer structure is subject to a slow process of structural reorganisation making the conductivity loss irreversible. Moreover, in conditions of deep dehydration, the mechanical characteristics of the membrane and in particular the plastic reserve thereof steeply decay, with an intolerable increase of the damage frequency in form of porosities and micro-fractures especially localised in the regions of higher mechanical strain, such as for instance the edges and the optional irregularities of the electrode surface.

To prevent these problems, the prior art is substantially directed either to ensure the air feed humidification, which however, being not complete for the above mentioned reasons, softens the risks of dehydration without eliminating the same, or to employ electrodes provided with reduced porosity in the gas inlet region, capable of hindering the diffusion of the product water thus better preserving the membrane hydration, but at the cost of a performance loss and of non negligible complications in the production phase.

The inventors, on the basis of a wide testing, have surprisingly found that it is possible to make a fuel cell operate in a stable fashion in a wide range of current density as required by the practical applications, with voltages representative of good energy conversion efficiencies, with stoichiometric factors equalling those of common use in the prior art (indicatively comprised between 1.2 and 3) also at near-ambient pressure and with no pre-humidification of the air feed, if the air feed is pre-cooled below 35°C and preferably below 30°C, with an optimum value around 25±2°C. By stoichiometric factor, as known to the experts of the field, it is intended the ratio between moles of fed reactant and moles of reactant required by

the reaction stoichiometry.

The behaviour of a stack fed with non pre-humidified air cooled down to 26°C according to the invention and formed by ten fuel cells with 225 cm² active area, equipped with commercial electrodes provided with 30% platinum supported on Vulcan XC-72 supplied by E-TEK Division/De Nora North America and with Nafion 115 DuPont proton-exchange membranes in a former version, and 40 micron thick Gore membranes in a latter version (totally equivalent behaviour) with cooling cells crossed by demineralised water intercalated thereto, is shown in figure 1; curve (100) indicates the cell voltage trend (left-hand ordinate axis) and curve (200) indicates the concurrent power trend (right-hand axis). The data were obtained operating at low pressure (1.5 bar) and with stoichiometric factor limited to 2; nevertheless it may be observed how a voltage of 0.7 V (representative of an energy conversion efficiency of about 50% considered as a lower acceptable limit) can be obtained at a current density of 4 kA/m² corresponding to a specific power of 2.8 kW/m². This value of specific power allows containing the dimensions of commercial stacks within economically interesting limits.

Figure 2 is a comparison of the performances of the stack in figure 1 with those of a stack also working at 1.5 bar absolute but with the known parameters of the current technology, in particular with air feed pre-humidified at 80°C and stoichiometric factor of 2.5: the voltage and power curves are respectively indicated with (101) and (201). Surprisingly, the two performances show only marginal differences.

Without wishing the present invention to be bound to any particular theory, it may be assumed that if the air feed temperature is decreased to the specified values, the reduced water vapour tensions in the air inlet region substantially reduce the local evaporation rate and the amount of water that can be evaporated. Of course the air, moving across the fuel cells, progressively increases its temperature with a simultaneous increase of the water vapour tensions and with a progressive evaporation: however such evaporation results distributed along the cell active area. In other words, the merit of the present invention might be distributing the water evaporation avoiding the hazardous concentration thereof in limited areas as

occurs in the fuel cells operated according to the indications of the prior art.

Figure 3 shows the result of a series of tests carried out adjusting the cooling water temperature and/or flow-rate so as to vary the outlet exhaust air temperature up to the limit where a performance loss began to be noticed, likely associated to the onset of membrane dehydration. The tests were carried out at 25°C with a stoichiometric factor of 2. From the diagram it can be observed that the maximum temperature of the outlet exhaust air (ordinate value) compatible with a stable operation in time using the indicated stoichiometric factor is a function of the working pressure (abscissa value): if the limiting factor is effectively the onset of membrane dehydration the result of figure 3 is then unsurprising since lower air volumetric flow-rates correspond to higher pressures and hence, all other conditions being equal, the capacity of withdrawing vapour decreases, which permits increasing the outlet temperature. Wishing to limit the fuel cell working pressure to 1-1.5 bar absolute, it can be concluded that the temperature and/or flow-rate of the cooling water (or in the more general case of the coolant fluid) must be regulated so as to guarantee a maximum exhaust air outlet temperature of 60-70°C. The ambient or near-ambient pressure operation is particularly interesting under the system reliability standpoint, considering the fact that the employed machines, particularly the air feed fan, and the seals, particularly the stack perimetrical gaskets which have a very high overall linear development, result not too critical.

In figure 4 the variation of the stoichiometric factor (indicated as f_{lim} on the ordinate axis) is reported as a function of exhaust air outlet maximum temperature (value on the abscissa) and of the working pressure. In particular, curve (301) is relative to an absolute pressure of 1.1 bar, (302) to 1.2 bar, (303) to 1.3 bar, (304) to 1.4 bar, (305) to 1.5 bar, (306) to 2 bar. It can be noticed that for a given exhaust air maximum outlet temperature the stoichiometric factor increases as the working pressure increases. In fact, as already said, when the working pressure increases the volumetric flow-rate, and thus the water-withdrawing capacity of air flowing inside the fuel cells is decreased: it follows that increasing the stoichiometric factor, and consequently the air flow-rate, is allowed provided the critical condition

corresponding to a water withdrawal inducing membrane dehydration is not exceeded. For example with the maximum air outlet temperature fixed at 65°C the allowed stoichiometric factor results 1.6 at 1.1 bar absolute working pressure and 2.3 at 1.5 bar absolute. It is convenient to recall that to a higher stoichiometric factor corresponds a lower oxygen depletion of air crossing the fuel cells with a consequent performance improvement.

As regards the cooling water, it is necessary to maintain the flow-rate thereof within reasonable limits in order to contain the energy consumption for the circulation within acceptable values: this condition practically results in a temperature variation between fuel cell inlet and outlet of about 10-15°C (with inlet temperatures of about 45-60°C), corresponding to flow-rates around 25-40 litre/hour/m². In any case the cooling water outlet temperature results substantially coincident with that of exhaust air.

The fact that stable operation is possible with a non-humidified air feed, provided the same is pre-cooled, is certainly surprising and positive under the operation simplicity standpoint, however it is clear that the problem of how to effect such pre-cooling has to be posed, considering that in many applications typical of stacks there is no coolant available at suitable temperature. In fact, in the vast majority of cases the task of cooling systems comprised of fuel cell stacks is deputed to the ambient air, which in summertime and particularly in some geographic areas may reach values of 40-45°C. Assuming that a temperature difference of at least 10°C is required between cooling air and fluid to be cooled to limit the size of the thermal exchange equipment, one concludes that the minimum temperature that the fluid to be cooled may reach is around 50-55°C. This limit is acceptable for the cooling water which, as seen above, may have a temperature of 45-60°C at the fuel cell inlet. Nothing can be done of course as regards the air feed which must be pre-cooled to at least 35°C, and preferably at least 30°C, with an optimum value of about 25°C.

Figure 5 represents a scheme of realisation of a conditioning device capable of taking the air feed to the above temperature levels: (1) indicates the air feed aspiration tubing, (2) the fan whose purpose is to ensure the required flow-rate

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with a modest overpressure, indicatively from 1.1 to 1.5 bar absolute (the described scheme is applicable, although with lesser advantages, to systems operating under pressures of 2-5 bar absolute, in which case (2) is a suitable compressor), (3) the delivery tubing of air exiting the fan (or compressor), (4) a heat exchanger directed to cool down the air warming up in the fan (or compressor) (2) using ambient air (5), (6) is the air feed delivery tubing to the expander (7), for instance a rotating expander, in which the air pressure is partially reduced with production of mechanical work, that is transmitted to the fan (2), and with temperature decrease, (8) the delivery tubing to the fuel cell stack (9), and (10) the exhaust air outlet tubing.

The temperature level that can be reached in the expander is a function of the pressure in (8) to pressure in (6) ratio: for a given pressure in (8) (stack operating pressure) the temperature level attainable by expansion is only a function of pressure in (6) (practically the fan or compressor (2) outlet pressure) and of the temperature in (6), in its turn a function of the ambient air temperature, which in the most unfavourable conditions (design conditions) is assumed to be 40-45°C. In principle, very low temperatures can be achieved, even below 0°C, but this would require excessive pressures in (6) with unacceptable energy consumption. Moreover, as previously discussed, interesting results are already obtained with temperatures of about 25°C. Using this value as the optimal cooling level, the following data are obtained in the case of a 9 kW stack consisting of 100 fuel cells, each of 225 cm² active area, and 100 cooling cells intercalated thereto fed with demineralised water:

- pressure at the fan (2) aspiration: ambient pressure
- temperature at the fan (2) aspiration: 45°C max (worst case)
- pressure at the fan (2) delivery: 1.3 bar absolute
- temperature at the fan (2) delivery: 78°C
- temperature downstream the heat exchanger (4): 51°C
- pressure after expansion, coincident with stack (9) operating pressure: 1.05 bar absolute
- air temperature after expansion: 25°C

- power absorbed by the fan (2): 1.4 kW
- power generated by the expander (7) and transmitted to the fan (2): 0.7 kW
- net power required by the device: 0.7 kW (8% of stack power)

It may be noticed that the heat exchanger (4) represents no critical component for the system design, as it simply has to cool down the air-feed flow from a temperature at the fan outlet which in the worst of cases is lower than 80°C, to a temperature of delivery to the expander around 50°C (typically 50±3°C): this may be easily accomplished making use of a second ambient air flow as the cooling fluid, considering also the modest thermal content of the non-humidified air feed.

Figure 6 indicates how, wishing to maintain the temperature of the air-feed to the stack at 25°C, the compression work is characterised by a multiplying factor (indicated as Φ on the ordinate axis) which is a function of ambient temperature (on the abscissa) and of the stack working pressure: curve (401) is relative to an absolute working pressure of 1.05 bar, curve (402) to 1.1 bar, curve (403) to 1.5 bar, curve (404) to 2.0 bar. The data in the figure show that the device is particularly convenient at low values of stack working pressure.

Although the present invention was described making reference to a particularly preferred embodiment, the experts of the field will reckon that several changes and modifications may be made without departing from the spirit thereof, such changes and modifications being intended as encompassed in the domain wherein protection is claimed, as comprised in the scope of the invention.